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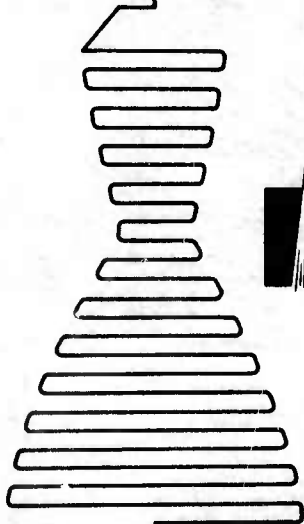
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(Unclassified Title)

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(1 June through 31 August 1964)

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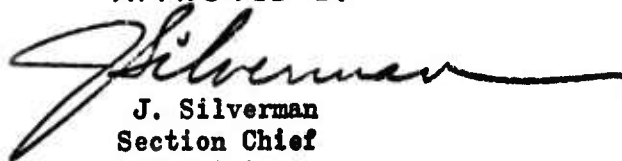
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FOREWORD

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The Responsible Engineer for this program is
Dr. D. Pilipovich. Dr. H. F. Bauer and Dr. C.
J. Schack are full-time associates.

ABSTRACT

Preparative routes to new interhalogen compounds
and their derivatives are being pursued. Initial
approaches utilized discharge techniques to evaluate
both fluorination and oxygenation of substrates such
as ClF_3, Cl_2O, and ClO_2. The reaction of solid FNO
with excited fluorine was demonstrated at -196 C with
the production of NF_3O. Similar procedures were
used in reacting Cl_2O and ClO_2 with F_2.

(Confidential Abstract)

CONTENTS

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INTRODUCTION

This report is the first quarterly report on a program directed toward the preparation of new inorganic oxidizers. The particular synthetic approaches to be utilized on this program are diverse, but all will be directed toward the realization of new interhalogen fluorides, oxyhalogen fluorides, and oxynitrogen fluorides. Initial studies to be described herein were designed to prepare new oxychlorine fluorides and utilized discharge techniques. The rationale for the use of the electric discharge is discussed both with respect to probable utility and in relation to other chemical approaches in synthesizing these materials.

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DISCUSSION

DISCHARGE REACTIONS

The selection of the electric discharge as a synthesis tool is based, to some extent, upon its successful application in preparing the new inorganic compounds ClF_5 and NF_3O (Ref. 1 and 2). These compounds are both simple and symmetrical and reflect the type of molecule that will arise from subjecting the proper elemental mixture to a discharge. If more complex molecules are desired it would appear that the electric discharge as a synthesis tool has only a limited utility. This is particularly true if it is realized that the products from a discharge reaction will often be consistent with the most stable species arising from relatively stable radicals. Thus N_2 and F_2, when subjected to a discharge, give only NF_3 and not N_2F_4 or higher NF species such as N_3F_5.

However limited the use of the electric discharge may appear when used in a "conventional" manner, the fact remains that the ternary system $N_2-F_2-O_2$ does give products containing all three elements, i.e., NF_3O. The question immediately arises as to whether ClF_3O and ClF_5O can result from the ternary mixture $Cl_2-F_2-O_2$. This obvious analogy was tested by subjecting this mixture to a discharge at -80 C. No new compounds were observed using a $F_2-Cl_2-O_2$ ratio of 6:1:1. Products found were ClO_2, $FClO_2$, ClF_3, and ClF_5. Due to the accidental presence of air in the starting material, NO_2, FNO, FNO_2, and $ClONO_2$ also were formed. Additional experiments were carried out at -196 C, and in addition to the above products, Compound B (Ref. 1) was found. This compound was identified as WF_6 which arose from the attack by F_2 on the tungsten used to achieve the glass-to-metal seals in the discharge apparatus. These results are consistent with those previously obtained in the Rocketdyne laboratories in discharge reactions of Cl_2 and F_2 where O_2 was known, at times, to be an impurity.

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Subjecting mixtures of Cl_2, F_2, and O_2 to the electric discharge does not appear to be promising on the basis of the above results. It appeared that variations in the discharge technique may offer more versatility in product control than the techniques now employed. One method decided upon was to utilize a gas-solid reaction where the gas is some excited species such as F_2^* or O_2^*. The solid material is in essence a cold wall where excess energy can be readily dissipated. The essential difference from the previous experiments is that specific bond formation is sought by the interaction of an excited species with a readily oxidized material as opposed to an overall excitation followed by random and fortuitous recombinations. The following equations demonstrate the reactions considered:

$$ClF_3 + O^* \longrightarrow ClF_3O^* \longrightarrow ClF_3O + Q \qquad (1)$$

$$ClF_5 + O^* \longrightarrow ClF_5O^* \longrightarrow ClF_5O + Q \qquad (2)$$

$$FClO_2 + F^* \longrightarrow ClF_3O_2^* \longrightarrow ClF_3O_2 + Q \qquad (3)$$

$$Cl_2O + F^* \longrightarrow ClF_4OClF_4^* \longrightarrow ClF_4OClF_4 + Q \qquad (4)$$

$$ClF_3 + ClF_5O \longleftarrow$$
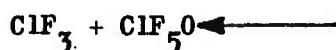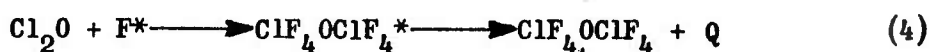
Thus, either O_2 or F_2 can be used for the above oxidations depending on the choice of the starting material. It should be noted that the excited species in the above equations are not represented as either radicals or ions. It is suspected that operation of the discharge below the ionization threshold will lead to radicals, and conversely, operation in the glow region will of course yield ions.

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The features of the solid-gas reaction at once became obvious for several reasons. First, it can be predicted that a higher degree of control can be exerted with regard to the structure of the products. This is dictated by the fact that one of the reactants, the solid, is the wall at which immediate dissipation of excess energy is anticipated. This is particularly important when it is realized that wall reactions enhance product formation in a discharge reaction. Subsequently, another feature is suggested in that higher yields of complex moieties may be realized. It should be recalled (Ref. 2) that in the discharge preparation of NF_3O from various gas mixtures the same low yields were obtained for the starting material combinations NF_3-O_2, $N_2-O_2-F_2$, and N_2-OF_2. This is no doubt based upon the statistical nature of a favorable combination of the excited F, N, and O to give the desired product.

To test the above assumptions, a model reaction was selected for study at -196 C. The desired reaction is:

$$FNO + F^* \longrightarrow F_3NO^* \longrightarrow F_3NO + Q \qquad (5)$$
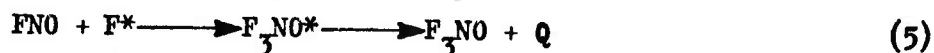
The use of FNO was selected because it not only has an oxidizable "central" atom but it should give the known compound NF_3O. The apparatus used was a U-shaped Pyrex discharge tube connected to a glass U-trap. Both were maintained at -196 C, and a constriction was placed in the trap about 10 inches downstream from the discharge zone. Nitrosyl fluoride was then condensed at the constriction, and F_2 was introduced into the discharge tube at a pressure below 50 millimeters.

Examination of the products in the trap showed NF_3O to be present, representing a 5-percent conversion of the FNO. A separate experiment, a control without FNO, yielded no NF_3O in the trap. The control was carried out in view of the fact that the F_2 supply often is contaminated

with small amounts of air. Subsequent experiments showed the FNO (s)-F* reaction to be reproducible. In view of the moderate success with the model selected, it appeared desirable to extend it to halogen oxides.

The selection of reactants in seeking routes to new F, Cl, and O species is quite limited. Prime consideration should be given to the valence of the "central" atom. On this basis, then, all chlorine (VII) species do not appear to be desirable since neither oxidations can occur nor is the replacement of O on chlorine probable. Consequently, perchloryl fluoride does not appear to be a suitable precursor for discharge studies. The chlorine compounds which meet the imposed requirements are $FClO_2$ (or ClO_2) and Cl_2O. Each can be envisioned as giving rise directly to the sought oxychlorofluorides:

$$Cl_2O \longrightarrow ClO\cdot + 1/2\ Cl_2 \tag{6a}$$

$$F\cdot + ClO\cdot \longrightarrow FClO \tag{6b}$$

$$FClO + F_2 \longrightarrow ClF_3O \tag{6c}$$

The reaction of Cl_2O as written proceeds through the rupture of a ClO bond which requires little energy in Cl_2O. The photodecomposition of chlorine monoxide proceeds initially according to the first step of Eq. 6a as does the chlorine-atom sensitized decomposition (Ref. 3).

To extend fluorination to halogen oxides, the selected precursors were subjected to conditions similar to those in the FNO(s)-F* experiments. For example, chlorine monoxide was frozen at -196 C on the reactor wall just downstream from the glow discharge electrodes. Fluorine passing between the electrodes is converted to fluorine atoms. These radicals are then able to bombard the solid reactant and effect fluorination.

By maintaining starting materials and products at -196 C, side reactions are minimized and hence the possibility of conversion to new energetic species is maximized.

In extending the solid-gas reaction to chlorine systems, two electrical discharge tubes have been employed. The first design maintained the Cl-O compound to be attacked at -196 C but left the electrodes above the bath where they were cooled by an air blower.

Chlorine monoxide was reacted twice with essentially the same result. All of the Cl_2O was used up, but the only ClO species formed was ClO_2. Also formed were Cl_2 and much SiF_4. The chlorine dioxide and chlorine probably arose directly from the decomposition of Cl_2O.

$$Cl_2O \longrightarrow ClO\cdot + Cl\cdot$$

$$ClO + Cl_2O \longrightarrow ClO_2 + 2Cl\cdot \qquad (7)$$
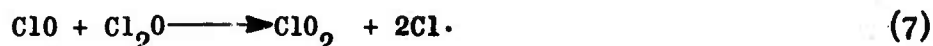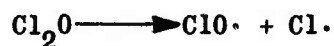
Initiation of this sequence by F atoms comparable to the known Cl atom process is possible. A chain radical reaction promoted by the product Cl atoms makes fluorine necessary only for initiation and not propagation. Thus, small amounts of ClF could have been formed but not detected.

Air contamination in one run was noted by the production of a small quantity of chlorine nitrate. This again is a well-characterized product of ClO radical reactions:

$$ClO\cdot + NO_2\cdot \longrightarrow ClNO_3 \qquad (8)$$

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Due to difficulties with the method originally selected for the preparation of $FClO_2$, ClO_2 was present as an impurity. Nevertheless, since ClO_2 is the precursor of $FClO_2$ it was expected that it would not adversely affect the reaction. In fact, fluorination of ClO_2 would itself indicate that suitable fluorination conditions were being approached.

Using this mixture in the solid phase, it was found that the discharge reaction resulted in consumption of the $FClO_2$ but not the ClO_2. The products were $FClO_3$ and SiF_4, in addition to the ClO_2. The conversion of chloryl fluoride to perchloryl fluoride is certainly not the result of fluorination, and the failure of the ClO_2 to be fluorinated leads to the conclusion that fluorination conditions were lacking.

The formation of appreciable amounts of SiF_4 using this technique can account for the findings. The activated fluorine may react with the glass of the tube around the electrodes too fast to allow sufficient amounts to reach the intended reaction zone. In addition, oxygen that is liberated by the conversion of the silica to SiF_4 may be responsible for the oxidation of $FClO_2$ to $FClO_3$.

So severe was the etching of the apparatus near the electrodes and the thermal strain encountered during operation, that the discharge tube cracked after several experiments. A newly designed system was fabricated in which both electrodes and substrates could be immersed in a liquid nitrogen bath. This tube has shown only limited etching after several experiments.

Again utilizing Cl_2O as the starting material, three experiments were conducted. Two distinct results were obtained depending upon the purity of the fluorine. In the absence of air impurity, most of the chlorine monoxide was reacted after 20 minutes. The yield of $FClO_2$, ClO_2, and

ClF_5, along with a trace of SiF_4, demonstrated that fluorination had been effected. Chlorine dioxide was formed from Cl_2O as shown earlier. Chloryl fluoride and chlorine pentafluoride resulted from the reaction of fluorine with the ClO_2 and Cl atoms, respectively. Presumably, Cl atoms are generated from the decomposition of Cl_2O, as pointed out earlier.

When air-contaminated fluorine passed through the discharge, the product composition was altered. As expected, ClO_2 and trace amounts of SiF_4 were formed. However, no $FClO_2$ was observed. Furthermore, appreciable yields of $ClNO_3$, ClF_5, and NF_3 were noted. These molecules are all known to result from the glow discharge reaction of the appropriate elements. The important point derived from the experiment is that fluorination of Cl in Cl=O bonds is much more difficult to achieve than is the corresponding reaction of other radical atoms or groups. Thus, although these are available, the active fluorine is so effectively added to them that an insufficient amount remains to promote the desired new species.

Pure $FClO_2$ and pure F_2 now appear to give the most promise of attaining the proposed objective via discharge reaction. Experiments with recently available chloryl fluoride of the required purity are in progress.

In both reactions of Cl_2O with air-contaminated fluorine it was observed that NF_3O was produced from the reaction products during a second warming from liquid nitrogen temperature. This was accompanied by the production of some noncondensible gas. It appears probable that the NF_3O results from the interaction of a trace of FNO and the decomposition products of O_2F_2, which is known to form in an F_2-O_2 discharge reaction (Ref. 3). Further clarification of this point is necessary.

Other Routes to FClO Species

It was proposed that high-pressure fluorinations would be carried out in attempting to pre$_x$are compounds such as ClF_3O_2, ClF_5O, etc. For example, the direct fluorination under pressure of $FClO_2$ and ClO_2 had been proposed. Since the proposal was submitted, these pressure fluorinations have been attempted without spectacular results (Ref. 4). Therefore, no pressure fluorinations of ClO species are contemplated at the present time.

The hydrolysis of ClF_5 has been shown at Rocketdyne not to lead to new ClFO species, particularly ClF_3O (Ref. 5). This was somewhat surprising in that the reaction was assumed to be a stepwise process, i.e.,

$$ClF_5 + H_2O \longrightarrow ClF_3O + 2 \ HF$$

$$ClF_3O + H_2O \longrightarrow FClO_2 + 2 \ HF \tag{9}$$

It would appear that either ClF_3O is more reactive to H_2O than ClF_5 or that it readily disproportionates to other products such as ClF_5 and $FClO_2$. This species will be sought with attention to mode of reaction in the case of pure ClF_5 or by studying the hydrolysis of ClF_4^+ salts.
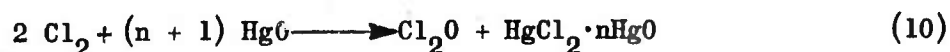
EXPERIMENTAL

PREPARATION OF Cl_2O AND $FClO_2$

Chlorine monoxide was prepared fresh from the reaction of chlorine gas diluted with nitrogen and freshly precipitated red mercuric oxide (Ref. 6).

$$2\ Cl_2 + (n + 1)\ HgO \longrightarrow Cl_2O + HgCl_2 \cdot nHgO \tag{10}$$

Storage of Cl_2O in glass ampoules at -196 C led to the slow formation of ClO_2.

Chloryl fluoride was at first synthesized by the reaction of perfluoro-acetic anhydride and chlorine pentafluoride.

$$ClF_5 + 2\ (CF_3CO)_2O \longrightarrow 4\ CF_3COF + FClO_2 \tag{11}$$
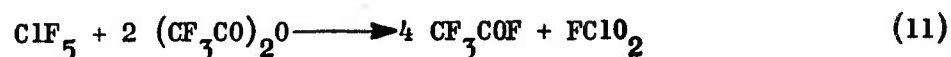
The reaction was carried out in a stainless-steel bomb at ambient temperature. However, the slow rate of the reaction was found to limit the yield of $FClO_2$. The chloryl fluoride produced was partially decomposed upon prolonged contact with the metal to give ClO_2. Also, the large amount of byproduct perfluoroacetyl fluoride required a lengthy separation from the $FClO_2$.

A more practical synthesis of this material is the reaction of silver oxide and chlorine pentafluoride. Again, using a stainless-steel reactor at ambient temperature, it has been possible to obtain a 55-percent yield of $FClO_2$. The only other volatile products are noncondensible at -196 C and hence easily removed.

DISCHARGE APPARATUS

The glow discharge tube was constructed of Pyrex with ..cuum stopcocks at inlet and outlet sides. The electrodes were copper and were sealed in the glass with gaps of 2 and 6 inches, respectively, in the two reactors. With the outlet stopcock barely opened, fluorine was passed through the fully opened inlet stopcock and maintained at 20 to 50 millimeters pressure. Duration of the discharge in all cases was approximately 20 minutes. Power was supplied by a 15-kilovolt luminous-tube transformer.

At the termination of each discharge reaction, the cooling bath was removed from the tube, and all volatile material was transferred to the vacuum line. Vacuum fractionation was conducted in a metal-Teflon system. Infrared spectra were taken on a PE 127 Infracord with the gaseous samples in a 5-centimeter monel cell fitted with silver chloride windows.

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